

A Contribution to the Knowledge of Dicarbonyl Cuprous Chloride.

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES
OF THE JOHNS HOPKINS UNIVERSITY

—BY—

WILLIAM APP JONES

1898

EASTON, PA.:
THE CHEMICAL PUBLISHING COMPANY
1899.

A Contribution to the Knowledge of Dicarbonyl Cuprous Chloride.

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES
OF THE JOHNS HOPKINS UNIVERSITY

—BY—

WILLIAM APP JONES

1898



EASTON, PA.:
THE CHEMICAL PUBLISHING COMPANY
1899.



Digitized by the Internet Archive
in 2026

CONTENTS.

Introduction.....	5
Preparation of material	
1. Cuprous chloride.....	6
2. Carbon monoxide	7
Preparation of dicarbonyl cuprous chloride.	7
Analysis of the compound	
1. Decomposition method	8
2. Absorption method.....	9
Behavior of compound under reduced pressure	
1. Compound in dilute hydrochloric acid	13
2. Compound in water	15
3. Compound in concentrated acid	16
Absorption of carbon monoxide by cuprous chloride in pyridine.....	16
Behavior of compound under increased temperature.....	18
Action of oxygen on dicarbonyl cuprous chloride	20
Action of chlorine.....	21
Action of hydrogen	22
Action of nitrogen	23

DISCUSSION OF RESULTS.

Action of oxygen on dicarbonyl cuprous chloride	23
The constitution and chemical nature of dicarbonyl cuprous chloride.	24
Effect of pressure changes on the molecular weight of compounds....	25
The disruptive influence of reduced pressure	26
Effect of a solvent on dissociating tension	26
Inorganic compounds containing carbon monoxide.....	27
Conclusions	29
Biographical.....	30

ACKNOWLEDGMENT.

The present work was undertaken at the suggestion of Professor Remsen, and his constant interest and advise have been of the greatest value.

I wish to thank him most sincerely for instructions received both in the lecture-room and laboratory; I feel especially indebted to him for the high ideals, not of chemistry alone but of life as well, which personal contact with him cannot fail to inspire.

My thanks are also due Professors Morse and Clark and Doctor Mathews for the instruction received at their hands.

A Contribution to Our Knowledge of Dicarbonyl Cuprous Chloride.

BY WILLIAM APP JONES.¹

INTRODUCTION.

In attempting to determine the free oxygen in illuminating gas by means of an ammoniacal solution of cuprous chloride, Leblanc, Stas, and Doyère² observed that a large quantity of carbon monoxide and ethylene were also absorbed.

Leblanc then showed that carbon monoxide is absorbed by a hydrochloric acid solution of cuprous chloride, easily and with only a very slight rise in temperature, and the same was found true for an ammoniacal solution. He believed that in both cases the proportion of carbon monoxide to cuprous chloride was 1 : 1.

Leblanc also noticed that by an elevation of temperature or by a removal of the atmospheric pressure from these solutions the carbon monoxide was given off as such, and that ammoniacal solutions of the cuprous salts in general have the power to absorb this gas. He did not succeed in isolating any definite compounds from these solutions.

In 1856 Berthelot³ succeeded in isolating the compound formed by passing carbon monoxide through a cold saturated solution of cuprous chloride in concentrated hydrochloric acid. He obtained beautiful pearly plates which altered very rapidly in the air, making it impossible to prepare them for analysis without at least some loss of carbon monoxide. The

¹ The work, an account of which is here given, was undertaken at the suggestion of Professor Remsen and carried out under his guidance. The article formed the dissertation submitted by the author to the Board of University Studies of the Johns Hopkins University for the degree of Doctor of Philosophy, June, 1898.

² *Compt. rend.* (1850), **30**, 483.

³ *Ann. chim. phys.* [3], **46**, 488.

figures obtained by his analyses approximated those required by the formula $4\text{Cu}_2\text{Cl}_2 \cdot 3\text{CO} \cdot 7\text{H}_2\text{O}$, but since the compound alters so rapidly he believed it to be $\text{Cu}_2\text{Cl}_2 \cdot \text{CO} \cdot 2\text{H}_2\text{O}$. Evidently this formula is based upon very unsatisfactory evidence, and the present work was undertaken to determine more accurately, if possible, the composition of the substance, to study its conduct under different conditions of temperature and pressure, and to determine the chemical activity of the carbon monoxide at the moment of its liberation.

PREPARATION OF MATERIAL.

Cuprous Chloride.

This was prepared by the action of *aqua regia* on copper turnings—the latter being in excess. In its preparation about half a liter of concentrated hydrochloric acid was poured into a flask containing 300–350 grams of the copper turnings, and the acid heated almost to boiling. Small quantities of concentrated nitric acid were then introduced from time to time and the heating continued for half an hour, when the hot solution was quickly filtered through asbestos and the cuprous chloride precipitated in the form of a fine white powder by the addition of several liters of cold water. The precipitate was then filtered off quickly and washed from acid, the final washings being made with glacial acetic acid. The material was at once dried in an air-bath, at a temperature of 115° – 125° C., for twelve hours. Proceeding in this way it is possible to obtain cuprous chloride perfectly dry and white, and a specimen kept for six months in a glass-stoppered bottle suffered no change in color. The analysis of the material gave the following results:

I. 0.2012 gram material gave 0.1607 gram CuO.

II. 0.2112 gram material gave 0.1692 gram CuO.

	Calculated for Cu_2Cl_2 .	I.	Found.	II.
Cu	64.06	63.72		63.94

Preparation of Carbon Monoxide.

The carbon monoxide used in most of the experiments was prepared by the action of sulphuric acid on potassium ferrocyanide, though comparative experiments were made with carbon monoxide obtained by the action of sulphuric acid on formic acid. In both cases the gas was passed through four or five wash-bottles, containing a concentrated solution of caustic potash and, when all the air had been displaced, it was collected in a glass gasometer.

Preparation of Dicarbonyl Cuprous Chloride.

In preparing this compound the cuprous chloride was placed in a small balloon flask, which in turn was immersed in ice-water. The flask was tightly fitted with a three-hole rubber stopper; through one opening a small dropping funnel was passed, and through the others glass tubes, provided with stop-cocks and bent at right angles, one of which was connected with a gas burette, the other with a suction-pump. The dropping-funnel and the tube leading to the gas burette were closed, connection made with the pump, and the flask exhausted. The connection with the pump was closed and enough hydrochloric acid introduced through the dropping-funnel to form a thin paste with the cuprous chloride. The tube leading to the gas burette, which contained carbon monoxide, was then opened and the absorption flask alternately shaken and immersed in ice-water. The absorption, which is at first quite rapid, toward the end becomes very slow, and only after several hours is it complete; frequent shaking is absolutely necessary.

The absorption being complete, ice-water was added, and the crystals which separated were quickly filtered and washed with ice-water, and then pressed between sheets of drying-paper with a previously cooled spatula. Unless the washing and drying has been done *very* quickly the white plates will have become a green paste, and in any case there will be a slight alteration.

Analysis of the Compound.

Decomposition Method.—As shown above, it is impossible to dry and then weigh the compound for analysis. In the first instance the material was washed and dried as quickly and thoroughly as possible, and then decomposed by an elevation of temperature, the products being either measured or weighed.

The apparatus for the decomposition consisted of a small bulb of about 6 cc. capacity, into which the compound was introduced. This bulb was provided with a two-hole rubber stopper: through one opening was passed a small glass tube, bent at right angles, which extended to the bottom of the flask, and was connected with a calcium chloride tube. This was closed during the decomposition.

A similar glass tube was introduced through the other opening, which extended just below the stopper, and was connected with a weighed calcium chloride tube in which the water given off by the decomposition of the compound was collected. This tube was protected by another calcium chloride tube, the latter being connected with a gas-measuring tube in which the carbon monoxide was to be collected. During the decompositions the little bulb containing the material was immersed to a given-point in a water-bath maintained at 80° C., and blank determinations were previously made to ascertain the correction to be applied to the volume of carbon monoxide collected, the correction being the expansion of the gas in the bulb.

The compound was prepared as previously described, dried very quickly between sheets of drying-paper, and at once transferred to the decomposition bulb, which had previously been weighed. The stopper was at once inserted and connection made with the weighed calcium chloride tube, the protecting calcium chloride tube, and the gas measuring tube. The decomposition bulb was placed in the water-bath, and a temperature of 80° C. maintained until there was no change in the volume of gas collected. This volume was corrected for temperature, pressure, water-vapor, and

for the expansion of the gas in the decomposition-bulb. The volume of carbon monoxide having been ascertained, the measuring-tube was disconnected and dry carbon dioxide pressed through the calcium-chloride tube previously closed, and the tube leading to the bottom of the decomposition-flask. This was continued until there was no change in the weight of the weighed calcium-chloride tube, when a final weighing of this tube and the decomposition-bulb was made, giving respectively the weight of the water and cuprous chloride in the compound. From the volume of carbon monoxide collected, its weight was calculated.

While this method is theoretically very simple, it is in reality very difficult on account of the extreme instability of the compound, which makes it almost, if not quite, impossible to dry it without some decomposition. While the method is rather unsatisfactory in the results obtained, yet it was the only one by which it was possible to determine the amount of water present.

The results of three analyses are given on page 10.

Absorption Method.—This method was also employed, as the results obtained were found to be more accurate than those obtained by the former method. From 1 to 2 grams of cuprous chloride were carefully weighed and introduced into an absorption bulb, similar to that described on page 289. The bulb was then closed, immersed to the mark in ice-water, and exhausted. The exhaustion being complete, connection with the pump was closed, enough concentrated hydrochloric acid introduced to form a thin paste with the cuprous chloride, the connection with the gas tube opened, and carbon monoxide allowed to enter, and the volume of gas in the measuring tube was quickly noted as soon as atmospheric pressure was reached in the absorption bulb. The bulb was then alternately shaken and immersed in ice-water until absorption was complete. This required about three hours, and toward the end of this time the flask must be shaken almost constantly. In some instances the bulb was kept in ice-water for

I.			II.			III.		
Cu_3Cl_2	0.3280 gram	= 60.78 per cent	0.2180 gram	= 62.21 per cent	0.2170 gram	= 62.41 per cent		
H_2O	0.1220 "	= 22.61 "	0.0740 "	= 21.11 "	0.0750 "	= 21.57 "		
CO	0.0896 "	= 16.60 "	0.0584 "	= 16.67 "	0.0557 "	= 16.02 "		
Total	0.5396 "	= 99.99 "	0.3504 "	= 99.99 "	0.3477 "	= 100.00 "		

Same results calculated in terms of Cu_3Cl_2 and CO for comparison with those recorded on page 293.

I.			II.			III.		
Cu_3Cl_2	0.3280 gram	= 78.54 per cent	0.2180 gram	= 78.87 per cent	0.2170 gram	= 79.57 per cent		
CO	0.0896 "	= 21.45 "	0.0584 "	= 21.13 "	0.0557 "	= 20.42 "		
Total	0.4176 "	= 99.99 "	0.2764 "	= 100.00 "	0.2727 "	= 99.99 "		

several days, being shaken at intervals, but no gas was absorbed after the first three hours, when this part of the operation had received the proper treatment.

Determinations were also made to see if the strength of acid used had any influence on the amount of carbon monoxide absorbed. It was found to have no effect, except that the absorption was the more rapid the more concentrated the acid used. This fact is doubtless due to the greater solubility of both compounds in the stronger acid.

These results led me to try pure water, and, while the absorption is very slow, exactly the same amount of carbon monoxide is absorbed as when hydrochloric acid is used.

When the bulb containing dicarbonyl cuprous chloride is heated to 60° or 70° C., exactly the same amount of carbon monoxide is given off as was originally absorbed. On cooling the bulb it is exactly reabsorbed, and this operation can seemingly be repeated indefinitely. Dry cuprous chloride does not absorb dry carbon monoxide.

I give below four analyses in the order in which they were made :

	Weight Cu_2Cl_2 .	Weight CO absorbed.	Per cent CO.	Remarks.
IV.	2.0006	0.5437	21.37	Cu_2Cl_2 in water
V.	1.0045	0.2703	21.20	Cu_2Cl_2 in 1HCl : 4H ₂ O
VI.	1.0069	0.2733	21.35	Cu_2Cl_2 in 1HCl : 2H ₂ O
VII.	1.0027	0.2749	21.51	Cu_2Cl_2 in conc. HCl.

I am aware that there is one considerable source of error in this method. The compound formed, as well as the cuprous chloride, is insoluble in water, and only slightly soluble in hydrochloric acid, so that no matter how long the absorption is continued nor how vigorously the bulb is shaken, some unchanged cuprous chloride will always be enclosed in the compound formed, causing the percentage of gas absorbed to be slightly low. The percentage of carbon monoxide required by different formulas is as follows :

$\text{Cu}_2\text{Cl}_2.\text{CO}$	requires	$\text{CO} = 12.41$
$4\text{Cu}_2\text{Cl}_2.7\text{CO}$	"	$\text{CO} = 19.91$
$5\text{Cu}_2\text{Cl}_2.9\text{CO}$	"	$\text{CO} = 20.37$
$6\text{Cu}_2\text{Cl}_2.11\text{CO}$	"	$\text{CO} = 20.66$
$12\text{Cu}_2\text{Cl}_2.23\text{CO}$	"	$\text{CO} = 21.40$
$\text{Cu}_2\text{Cl}_2.2\text{CO}$	"	$\text{CO} = 22.13$

It is evident that the formulas considered probable by Leblanc ($\text{Cu}_2\text{Cl}_2.\text{CO}$) and the one assigned to the compound by Berthelot ($\text{Cu}_2\text{Cl}_2.\text{CO}.2\text{H}_2\text{O}$) cannot be entertained. The percentage of carbon monoxide in $\text{Cu}_2\text{Cl}_2.\text{CO}$ is only 12.41; the average of more than fifty determinations made by me, and varying from one another by only a few tenths of a per cent, is about 21.4 per cent.

Exactly 21.4 per cent of carbon monoxide is removed by the formula $12\text{Cu}_2\text{Cl}_2.23\text{CO}$. While such complex compounds are not unknown in inorganic chemistry, certainly they are quite rare, and while the percentage of carbon monoxide required by $\text{Cu}_2\text{Cl}_2.2\text{CO}$ is 22.13, yet there is a constant error in both methods, causing the results to be slightly low, so that it seems to me fair to accept the formula $\text{Cu}_2\text{Cl}_2.2\text{CO}$ as highly probable.

As regards the proportion of water present, we must rely entirely on the decomposition method. While this was found to be not as accurate as could be desired, yet there is a certain rough agreement. In three successive determinations the percentages of carbon monoxide found were 21.45, 21.13, and 20.42. These results show that the compound had slightly decomposed in drying, yet the average percentage of carbon monoxide (21.0) is only slightly below the average obtained by the other method (21.4). Keeping the proportions $\text{Cu}_2\text{Cl}_2.2\text{CO}$ constant and varying the proportion of water, we obtain :

$\text{Cu}_2\text{Cl}_2.2\text{CO}.3\text{H}_2\text{O}$	contains	$\text{H}_2\text{O} = 17.55$	per cent.
$\text{Cu}_2\text{Cl}_2.2\text{CO}.4\text{H}_2\text{O}$	"	$\text{H}_2\text{O} = 22.11$	"
$\text{Cu}_2\text{Cl}_2.2\text{CO}.5\text{H}_2\text{O}$	"	$\text{H}_2\text{O} = 26.19$	"

The average percentage of water was found to be 21.76 (page 10), only 0.35 per cent lower than required by $\text{Cu}_2\text{Cl}_2.2\text{CO}.4\text{H}_2\text{O}$. On the other hand it is 4.21 per cent higher than

required by $\text{Cu}_2\text{Cl}_2 \cdot 2\text{CO} \cdot 3\text{H}_2\text{O}$ and 4.43 per cent lower than required by $\text{Cu}_2\text{Cl}_2 \cdot 2\text{CO} \cdot 5\text{H}_2\text{O}$. This makes it seem highly probable that the composition of dicarbonyl cuprous chloride is expressed by the formula $\text{Cu}_2\text{Cl}_2 \cdot 2\text{CO} \cdot 4\text{H}_2\text{O}$.

Behavior of Dicarbonyl Cuprous Chloride under Reduced Pressure.

Leblanc pointed out that this compound loses carbon monoxide when the atmospheric pressure is removed, yet no exact statement has been made in regard to this point, so experiments were undertaken with this object in view.

The compound was prepared in a bulb of 5 cc. capacity. This bulb was provided with a dropping-funnel having a three-way stop-cock, so that it could be disconnected or connected with a gas measuring tube containing carbon monoxide, and with a Sprengel pump. A manometer was connected with the tube leading to the pump. Blank experiments were made to ascertain the correction, due to the expansion of the air in the bulb and tubes. For this purpose the bulb, containing the same amount of water as that used in the actual experiments, was immersed to the mark in ice-water, and the pump started. The gas pumped out at different pressures was collected in a measuring tube and corrected for temperature, pressure, and water vapor. These corrections are :

Pressure. mm.	Vol. air collected. cc.	Pressure. mm.	Vol. air collected. cc.
460	29.9	130	60.0
360	39.0	100	63.2
260	48.2	60	66.4
160	57.6	40	68.0

The compound having been prepared in the usual manner, it was only necessary to close the connection with the gas burette and open the stop-cock leading to the pump.

The first series, in which dilute acid was used, is as follows :

Table I.

0.5058 gram Cu_2Cl_2 (in $1\text{HCl} : 12\text{H}_2\text{O}$) absorbed 0.1364 gram (109 cc.) Co (= 21.24 per cent).

Pressure. mm.	Total vol. gas. cc.	Correction. cc.	CO given off. cc.	Decomposed. Per cent.
460	29.99	29.9	0.09	0.07
360	39.40	39.0	0.40	0.35
260	49.20	48.2	1.00	0.87
160	59.80	57.6	2.20	1.92
135	170.16	59.3	111.86	98.12
40	182.01	68.0	114.01	100.00

At each pressure given above the pump was stopped for twenty-four hours to see that the reading was constant, and at the end of a week, at a pressure of 160 mm., only 2.2 cc. of gas had been given off. When the pressure was lowered to 135 mm. bubbles of gas were given off rapidly, and at the end of nine days more 111.86 cc. of gas had been given off. When a constant reading had been obtained the pressure was lowered to 40 mm. and this maintained for a week, but only 2.15 cc. of gas were given off in this time.

Table II.

0.4910 gram Cu_2Cl_2 (in 1HCl : 12H₂O) absorbed 0.1319 gram (105.5 cc.) CO (= 21.17 per cent).

Pressure. mm.	Total vol. gas. cc.	Correction. cc.	CO given off. cc.	Decomposed. Per cent.
460	30.2	29.9	0.3	0.28
360	39.4	39.0	0.4	0.37
260	49.5	48.2	1.3	1.21
160	59.6	57.6	2.0	1.87
135-125	165.6	59.3	106.3	99.42
40	274.9	68.0	106.9	100.00

These two decompositions are given as extremes, the first being exceptionally poor, the last slightly better than the average. In all cases slightly more gas was collected than originally absorbed. It was impossible to dispense with all rubber connections, and although these were kept well covered with shellac, one could hardly expect to prevent diffusion of air into the apparatus when such a low pressure was maintained for three weeks. It seems, therefore, that the compound made in dilute hydrochloric acid is not decomposed until the pressure is reduced to 135-125 mm., and that it is completely decomposed at this point.

Behavior of the Compound Made with Water.

The compound obtained by the absorption of carbon monoxide by cuprous chloride in water, was next submitted to reduced pressure.

Table I.

Co absorbed = 90.05 cc.

Pressure. mm.	Total vol. gas. cc.	Correction. cc.	CO given off. cc.	Decomposed. Per cent.
460	30.1	29.9	0.2	0.22
360	39.3	39.0	0.3	0.33
260	49.0	48.2	0.8	0.88
160	58.8	57.6	1.2	1.32
130	102.7	60.0	42.7	46.97
100	109.2	63.2	45.7	50.27
60	156.9	66.4	90.5	99.55
40	158.9	68.0	90.9	100.00

By way of explanation, it should be stated that in lowering the pressure from 760-160 mm. only 1.2 cc. of carbon monoxide were given off, but at 130 mm. the evolution of gas increased, and at the end of five days 42.7 cc., or 2.32 cc. less than half the amount absorbed, had been collected when the reading became constant. In lowering the pressure from 130-60 mm. only about 5 cc. of gas were given off, but at 60 mm. the evolution again increased and continued until the compound was decomposed.

Table II.

CO absorbed = 103.33 cc.

Pressure. mm.	Total vol. gas. cc.	Correction. cc.	CO given off. cc.	Decomposed. Per cent.
460	30.2	29.9	0.3	0.28
360	39.4	39.0	0.4	0.37
260	49.2	48.2	1.0	0.95
160	59.0	57.6	1.4	1.33
130	109.99	60.0	49.99	47.70
100	114.92	63.2	51.72	49.35
60	170.89	66.4	104.49	99.63
40	172.87	68.0	104.87	100.00
				cc.
Total vol. gas collected				104.87
" " " absorbed				103.33
Difference				1.54

	cc.
One-half vol. gas absorbed	51.66
Vol. gas given off at 130 mm.	49.99
Difference	1.67

It was noticed in these decompositions that a dark coating was formed in the bulb, having a metallic appearance when deposited slowly and in fine condition. This coating gave the copper test distinctly. The fact will be referred to later.

Behavior of the Compound made with Concentrated Hydrochloric Acid.

The results of one determination will show this behavior in a general way.

CO absorbed = 105.2 cc.

Pressure. mm.	Total vol. gas. cc.	Correction. cc.	CO given off. cc.	Decomposed. Per cent.
410	40.7	39.2	1.5	1.38
310	60.2	44.7	15.5	14.32
260	74.4	48.2	26.2	24.21
210	91.8	52.9	38.9	36.95
160	117.2	57.6	59.6	55.08
130	168.2	60.0	108.2	100.00

It will be seen from the above that in this instance decomposition begins at about 410 mm. pressure and gradually increases to 160 mm., when it increases more markedly until decomposition is complete at 130 mm.

This decomposition agrees with those in which dilute acid was used in that decomposition is complete at 130 mm.; it differs from both in that marked decomposition begins below 130 mm. The stronger the acid the greater the ease with which carbon monoxide is absorbed, and also giving off again under reduced pressure. These results are discussed and the decompositions expressed in the form of curves on page 28.

Absorption of Carbon Monoxide by Cuprous Chloride in Pyridine.

It was desired to test the effect of increased temperature on some compound of cuprous chloride and carbon monoxide. The compound made with water or hydrochloric acid is too

sensitive to heat to be studied with accuracy. W. Lang¹ has noted that cuprous chloride in pyridine has the power to absorb carbon monoxide; this compound was prepared and found to have the stability desired.

The method of preparation was similar to that described on page 7. No matter how carefully the bulb was exhausted, the instant the pyridine came in contact with the cuprous chloride, both assumed a deep-green color and the bulb became slightly warm. The material showed an annoying tendency to form small hard lumps, and it was necessary to heat to 60° or 70° C. to get these lumps broken and into solution. Complete solution was doubtful even then, as the liquid was so dark that it was impossible to see through it.

Having obtained a solution as nearly perfect as possible, the absorption of carbon monoxide was effected as in the former experiments. The compound formed appeared as shining white plates on the bottom of the bulb and, on the addition of ice-water, more of the material was precipitated. All attempts to filter and dry this compound failed, as the crystals instantly turn green in the air.

As the compound formed by the absorption of carbon monoxide by cuprous chloride in pyridine is too unstable to admit of drying it, recourse must be had to the absorption method. A large number of determinations were made, and below is given a series showing the extremes. The average tended rather to the higher than the lower percentage.

Weight Cu_2Cl_2 .	Weight CO absorbed.	Per cent CO.
1.0005	0.172637	14.71
0.2020	0.035630	14.98
0.2055	0.036319	15.00
0.4036	0.072710	15.26
0.4028	0.076182	15.90
0.2040	0.039030	16.05

It will be seen at once that the results vary quite widely, probably in consequence of the caking of the cuprous chloride, thereby making absorption incomplete. If the relation of cuprous chloride to carbon monoxide is a simple one, it is probably represented by the formula $2\text{Cu}_2\text{Cl}_2 \cdot 3\text{CO}$, since the

¹ Ber. d. chem. Ges., 21, 1584.

percentage of carbon monoxide, as determined, is undoubtedly low.

The percentages required by the simpler hypothetical compounds are the following :

$\text{Cu}_2\text{Cl}_2 \cdot \text{CO}$	requires	$\text{CO} = 12.41$
$2\text{Cu}_2\text{Cl}_2 \cdot 3\text{CO}$	“	$\text{CO} = 17.57$
$3\text{Cu}_2\text{Cl}_2 \cdot 5\text{CO}$	“	$\text{CO} = 19.15$
$\text{Cu}_2\text{Cl}_2 \cdot 2\text{CO}$	“	$\text{CO} = 22.13$

Behavior of the Compound under Increased Temperature.

The method of work was the following : Into a bulb of 25 cc. capacity a weighed quantity of cuprous chloride (about 0.403 gram) was introduced and the bulb closed with a two-hole rubber stopper. Through one opening was passed a dropping funnel and through the other a bent glass tube. The bulb was then exhausted and nitrogen allowed to enter until all air had been displaced, 5 cc. of pyridine introduced, connection made with a gas burette, and the bulb immersed to a given mark in a water-bath, the temperature of which was accurately regulated. As the temperature of the bath was raised, the gas expelled on account of expansion was collected and, at the desired points, the temperature was kept constant for an hour, when final readings were made. The corrections used in the determinations were as follows :

Temperature of bath.	Vol. gas collected. cc.	Temperature of bath.	Vol. gas collected. cc.
0°	0.000	60°	8.592
10°	1.869	70°	10.863
20°	2.849	80°	13.578
30°	3.917	90°	16.739
40°	5.164	100°	21.401
50°	6.767		

In the actual experiments it was always impossible to get off as much gas as was originally absorbed. This may have been influenced by a difference in the vapor-tension of the liquid in the blank and real determinations, or to a reaction between the pyridine and rubber connections, or between the pyridine and cuprous chloride. After each determination the bulb contained a coating of what seemed to be metallic copper, but more abundant than that mentioned previously (page

16). It is conceivable that this reaction had taken place to a slight extent:



If carbon dioxide was formed it was, of course, dissolved by the water in the gas burette, making the readings low.

In the experiments the compound was prepared as previously described, and the decompositions made as in the blank determinations.

Table I.

0.4036 gram Cu_2Cl_2 absorbed 0.0727 gram (= 58.144 cc. CO)CO (= 15.26 per cent).

Temperature.	Total vol. gas. cc.	Correction. cc.	CO given off. cc.	Decomposed. Per cent.
10°	2.717	1.869	0.848	1.45
20°	13.858	2.849	11.009	18.93
30°	22.283	3.917	18.366	31.58
40°	31.188	5.164	26.024	44.75
50°	40.012	6.767	33.245	57.17
60°	47.565	8.592	38.973	67.02
70°	54.571	10.863	43.708	75.17
80°	61.207	13.578	47.629	81.90
90°	68.824	16.739	52.085	89.57
100°	76.029	21.401	54.628	93.95

Table II.

0.4042 gram Cu_2Cl_2 absorbed 0.0702 gram (= 56.16 cc. CO)CO (= 14.79 per cent).

Temperature.	Total vol. gas. cc.	Correction. cc.	CO given off. cc.	Decomposed. Per cent.
10°	4.016	1.869	2.147	3.82
20°	11.849	2.849	9.000	16.02
30°	23.138	3.917	19.221	34.22
40°	28.158	5.164	22.994	40.94
50°	39.015	6.767	32.248	57.42
60°	47.934	8.592	39.342	70.05
70°	53.951	10.863	43.088	76.72
80°	61.831	13.578	48.253	85.92
90°	68.042	16.739	51.303	91.35
100°	74.595	21.401	53.194	94.71

These results are expressed in the form of curves on page 28.

Action of Oxygen on Dicarbonyl Cuprous Chloride.

These experiments were undertaken to determine whether or not the carbon monoxide possess unusual activity at the moment of liberation from the compound. When oxygen, free from carbon dioxide, is passed through dicarbonyl cuprous chloride, even at 0° , the compound instantly turns green, and the gaseous mixture when conducted through baryta water, shows the presence of carbon dioxide. The cuprous chloride contained no material which could give carbon dioxide, for, when oxygen was conducted through this material, suspended in water, and then through baryta water for several hours, not the least precipitate was formed.

Thinking that carbon monoxide might be alternately absorbed and given off, when a mixture of this gas and oxygen is allowed to pass through moist cuprous chloride at 0° , the following method of work was adopted: From 1 to 2 grams of cuprous chloride were placed in a flask and covered with water. This flask was provided with a two-hole rubber stopper, through each opening of which was passed a glass tube bent at right angles, one reaching just below the stopper and the other to the bottom of the flask. The stopper and tubes being in place, the flask was connected with a series of wash-bottles, so that the current of gas used passed first through two wash-bottles containing caustic soda, then through a baryta solution into the cuprous chloride. On issuing from this flask it passed through another bottle containing baryta water, which was protected from the air by a bottle containing a solution of caustic soda. At first pure oxygen was passed through this series for about two hours. The cuprous chloride became slightly green, and neither the baryta solution before or beyond the cuprous chloride flask showed any signs of cloudiness. Without disturbing the apparatus, carbon monoxide was mixed with the oxygen and, when the mixture had been passed for fifteen minutes, a coating began to appear on the entrance tube of the baryta bottle beyond the cuprous chloride flask. At the end of two hours a per-

ceptible precipitate had been formed, while the baryta solution before the cuprous chloride flask remained entirely clear. A determination of the barium carbonate showed that the carbon dioxide formed was less than 1 per cent of the carbon monoxide employed. This experiment was repeated several times, and always with the same result.

The passage of a mixture of oxygen and carbon monoxide over ferrous sulphate or chloride does not cause the formation of carbon dioxide.

Action of Chlorine on Dicarboxyl Cuprous Chloride.

If carbon monoxide possesses unusual activity at the moment of liberation from this compound, we should expect it to show this quite markedly in its conduct toward chlorine. If carbonyl chloride should be formed it would react with the water of crystallization in the compound.

The apparatus consisted of a flask for the preparation of the compound, which was provided with an inlet tube reaching to the bottom, and an outlet tube extending just below the stopper. The outlet tube was connected with a larger tube containing finely powdered antimony, which was in turn connected with a gas measuring tube containing caustic potash. In the preparation of the compound a flask of known size was employed, and the amount of carbon monoxide absorbed was accurately measured. The flask containing the compound was then connected with the antimony tube, and also with a chlorine generator, from which the air had been expelled as completely as possible. When the inlet tube, containing chlorine, was opened, the tube leading from the absorption flask and connected with the antimony tube and gas measuring tube was also opened. The moment the chlorine touched the crystals of dicarboxyl cuprous chloride they turned green and gave off bubbles of gas. The passage of chlorine was continued until all the material had gone into solution, showing complete oxidation of the cuprous chloride. The excess of chlorine was taken up by the antimony and any carbon dioxide formed was absorbed by the caustic soda, while the unchanged carbon monoxide was collected.

At the end of the operation the vessel originally containing

the dicarbonyl cuprous chlorine was filled with water, so as to drive over all the gas contained in it. Knowing the amount of carbon monoxide absorbed, as well as the capacity of the absorption bulb, and hence the volume of free carbon monoxide contained in it after absorption, it was only necessary to subtract the volume of gas collected from the sum of these two to determine the amount of carbon monoxide that had been changed. Blank experiments showed that powdered anti-mony has not the power of effecting union between carbon monoxide and chlorine. All experiments were performed in diffused daylight.

The rate of flow of the chlorine seemed to affect the amount of carbon dioxide changed, this being greater the slower the current. The same effect was produced by lowering the temperature, thus retarding the decomposition of the compound. For these reasons it was impossible to get entirely concordant results. Below I give an average series of determinations:

CO absorbed. cc.	CO collected. cc.	CO changed. cc.	Per cent changed.
63.2	62.4	0.8	1.26
54.1	52.0	2.1	3.88
69.0	68.4	0.6	0.86
78.6	76.6	2.0	2.54
77.2	73.1	4.1	5.31

From these results it seems that there is a slight reaction between the two gases, but if the carbon monoxide possesses unusual activity, we should expect a greater change than the above figures indicate.

Action of Hydrogen on Dicarbonyl Cuprous Chloride.

Since oxygen has the power to decompose this compound even at and below 0° , it seemed advisable to try the action of hydrogen. The compound was prepared in the usual manner, and the bulb containing it, still immersed in ice-water, was introduced into a system of gas wash-bottles, similar to that described on page 20. Hydrogen, prepared by the action of hydrochloric acid on pure zinc, and then washed with caustic potash, lead acetate, and potassium permanganate, was passed through the compound for eight hours. At the end of this time the crystals had in no way changed their

appearance, and the water contained in the wash-bottles, through which the gas passed on leaving the flask containing the compound, had neither taste nor odor, was neutral in reaction, and did not reduce Tollens' solution in the cold. The compound was then allowed to assume the room temperature, and finally decomposed by warming to 60° , but no change in the carbon monoxide could be detected.

Action of Nitrogen.

These experiments were conducted exactly as in the case of hydrogen. At 0° the compound was not affected by nitrogen, and when the bulb was warmed so as to drive off the carbon monoxide no change whatever could be detected in the latter.

DISCUSSION OF RESULTS.

Action of Oxygen on Dicarbonyl Cuprous Chloride.

There can be no doubt that when oxygen is passed into this compound at 0° it undergoes decomposition, and there is formed simultaneously a small amount of carbon dioxide. This carbon dioxide cannot be due to an impurity in the cuprous chloride, for oxygen passed through the same material gives us no carbon dioxide whatever. Neither can it be due to a peculiar activity of the oxygen brought about by the cuprous chloride through its oxidation, thus causing a splitting of the molecular into atomic or active oxygen, for, when a mixture of oxygen and carbon monoxide is passed through ferrous sulphate or chloride these compounds are oxidized, yet no carbon dioxide is formed. The oxidation of carbon monoxide by the action of oxygen on dicarbonyl cuprous chloride must be due to the activity of the carbon monoxide, or else it is brought about through the agency of the cuprous chloride.

While we have some evidence pointing to the fact that both elements and compounds are unusually active at the moment of their liberation, yet it is far from certain that this activity is a property of the element or compound *per se*. Both heat and electrical phenomena are possibly involved, so that at present we have no satisfactory explanation of the real or apparent activity of the nascent state. If the formation of car-

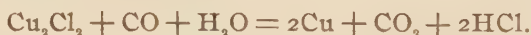
bon dioxide is due to the activity of the carbon monoxide, it is surprising that this activity is not expressed more strongly toward chlorine.

Drehschmidt has shown¹ that when an ammoniacal solution of cuprous chloride is used for the absorption of carbon monoxide, metallic copper is formed, this being due, as he thinks, to a reduction of the cuprous chloride by the carbon monoxide.

Winkler² shows that caustic potash causes the precipitation of metallic copper from a solution of cuprous chloride containing carbon monoxide; carbon dioxide is formed at the same time.

Winkler also points out³ that by the action of carbon monoxide on a solution of cuprous chloride and palladium chloride, palladium is precipitated and carbon dioxide formed, thus: $\text{PdCl}_2 + \text{CO} + \text{H}_2\text{O} = \text{Pd} + \text{CO}_2 + 2\text{HCl}$. In the absence of cuprous chloride this reaction takes place much more slowly.

As previously stated, in the decomposition of dicarbonyl cuprous chloride by reduced pressure, as well as in the decomposition of the pyridine compound by an elevation of temperature, a coating was formed which had the appearance of metallic copper and gave the test for copper. Considering these facts it seems probable that the formation of carbon dioxide is due to this reaction:



The Constitution and Chemical Nature of Dicarbonyl Cuprous Chloride.

As regards the structure of this compound I have no suggestion to offer. Formulas might be written to satisfy all the bonds of the elements involved, but there is no experimental basis for such a procedure. It seems fairly certain that its composition is represented by the formula $\text{Cu}_2\text{Cl}_2 \cdot 2\text{CO} \cdot 4\text{H}_2\text{O}$. Remembering that both cuprous chloride and carbon monoxide are unsaturated compounds, it does not appear unnatural that they should unite and mutually saturate each other. How the parts are united is a far more difficult question.

¹ Ber. d. chem. Ges., 20, 2754.

² Ztschr. anal. Chem., 28, 272.

³ Loc. cit., 274.

What is more important, and regarding which there is some strong evidence, is a consideration whether the compound is in reality a true chemical individual, an "atomic," as opposed to "molecular," compound. The material has a constant crystal form and luster. It is quite stable at low temperatures in the absence of active substances. If the temperature is elevated or the pressure greatly reduced, it undergoes decomposition, but in a manner similar to compounds, the atomic nature of which is not doubted. In confirmation of this I cite the following cases:

Effect of Pressure Changes on the Molecular Weight of Compounds.

It was observed by Naumann¹ that not only does the density of acetic acid vary with the temperature but also with the pressure, temperature remaining constant.

Acetic Acid—Temperature 100°.

Pressure. mm.	Density.	Pressure. mm.	Density.
393	3.44	168	3.01
342	3.37	156	2.98
258	3.17	130	2.94
232	3.12	92	2.76
186	3.06	77	2.66

Theoretical for $C_2H_4O_2 = 2.073$

" " $C_4H_8O_4 = 4.150$

Similar results were obtained at temperatures ranging from 78° – 185° , and the work confirmed by Ramsay and Young² through a much wider range of pressures.

The molecular weight of hydrofluoric acid as determined by Gore³ corresponds to the formula HF. The molecular weight, as determined by Mallet,⁴ at 30° C., is 39.32, almost exactly that required by H_2F_2 . By a more extensive investigation Thorpe and Hambly⁵ have shown that, at the ordinary temperature, the compound is to be expressed by the formula HF. On lowering the temperature the molecule becomes more complex and finally approaches H_2F_2 . The change in

¹ Ann. Chem. (Liebig), **155**, 325.

² Jour. Chem. Soc., **49**, 790.

³ *Ibid.*, **22**, 377.

⁴ Am. Chem. J., **3**, 189.

⁵ Jour. Chem. Soc., **53**, 765, and **55**, 163.

density is gradual, there being no sharp breaks, as this series of determinations shows.

Temperature.	Partial pressure. mm.	Vapor-density (H = 1).	Corresponding molec. weight.
32.0°	743	19.87	39.74
32.2°	686	17.89	35.78
31.8°	655	16.99	33.98
32.0°	603	15.41	30.82
32.5°	545	13.89	27.78
32.3°	498	13.27	26.54
31.9°	354	11.50	23.00
32.3°	353	11.39	22.78

Naumann has proved¹ in the case of nitrogen peroxide that for a given temperature the dissociation of N_2O_4 into NO_2 is greater the less the pressure.

Temperature.	Pressure. mm.	Dissociated. Per cent.	Temperature.	Pressure. mm.	Dissociated. Per cent.
18.0°	279	17.3	20.0°	301	17.8
18.5°	136	29.8	20.8°	153	29.3

The Disruptive Influence of Reduced Pressure on Chemical Combinations.

A striking example is afforded by the work of Lemoine on hydriodic acid.² He shows that, with constant temperature, the less the pressure, the smaller the amount of hydrogen and iodine in combination.

Pressure. Atmospheres.	Per cent free H.	Pressure. Atmospheres.	Per cent free H.
4.5	24	0.9	26
2.3	25	0.2	29

Boussingault has proved³ that while oxygen is absorbed by barium oxide at 450°, barium dioxide being formed, if the pressure is then removed, all the oxygen originally taken up is given off again. In other words, by means of a reduction of pressure this transformation is effected, $BaO_2 \rightarrow BaO + O$.

Effect of a Solvent on Dissociation Tension.

Gautier has shown⁴ that dry acid sodium carbonate is only very slightly dissociated in a vacuum of 10–20 mm. at 25°–30°.

¹ Ber. d. chem. Ges., **11**, 2045.

² *Ibid.* [5], **19**, 464.

³ Ann. chim. phys. [5], **12**, 145.

⁴ Bull. Soc. Chim., **26**, 115.

If the material is moistened the results are entirely different. When 5 grams of the material were dissolved in 20 grams of water and the solution placed in a vacuum of 300–400 mm. at 25° – 30° , at the end of four days the salt was dry and consisted of about 18.7 per cent NaHCO_3 and 81.3 per cent Na_2CO_3 . He found that water exerts the same influence on the dissociation of acid potassium carbonate, and Berthelot and André¹ obtained similar results with acid ammonium carbonate.

It is probable that a similar explanation is to be found for the differences in decomposition of dicarbonyl cuprous chloride. The material is insoluble in water, and in this instance the carbon monoxide is absorbed and given off with the greatest difficulty. It is soluble in hydrochloric acid, and similar to solutions of the acid carbonates of the alkalies, it is then decomposed much more easily. These decompositions can be readily compared by means of the curves on page 28. The break in the curve representing the decomposition of the compound made in water appears somewhat exaggerated. While there undoubtedly is a break, yet it extends only through a very short range of pressure—from about 130–160 mm.—so that a slight error in observation would lead to quite different results. I hardly think this slight irregularity sufficient reason for concluding that, when the compound is prepared in water, 1 molecule of carbon monoxide is united in a manner different from the other.

The decomposition by increased temperature of the compound made in pyridine is exactly similar to the decomposition of acetic acid and nitrogen peroxide, as can be seen from the curves.

Behavior of Inorganic Compounds containing Carbon Monoxide.

The compounds COPtCl_2 , $(\text{CO})_2\text{PtCl}_2$, and $(\text{CO})_3(\text{PtCl})_2$ (Schützenberger²) as well as COPdCl_2 , $(\text{CO})_2\text{PdCl}_2$, and $(\text{CO})_3(\text{PdCl}_2)_2$ (Fink³) can be converted one into another by changing the temperature and proportion of carbon monoxide present and all are decomposed by water, the compounds $(\text{CO})_2\text{PtCl}_2$, $(\text{CO})_3(\text{PtCl})_2$, $(\text{CO})_2\text{PdCl}_2$ and $(\text{CO})_3(\text{PdCl}_2)_2$,

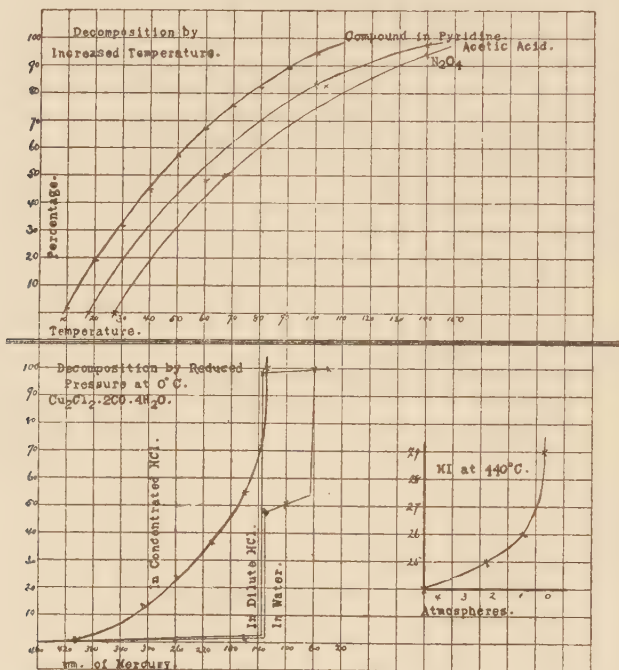
¹ Compt. rend., 103, 665 and 716.

² Ann. chim. phys. [4], 15, 100; and [4], 21, 350.

³ Compt. rend., 126, 646.

giving off part of their carbon monoxide as such—*e. g.*,
 $(\text{CO})_2\text{PtCl}_2 + \text{H}_2\text{O} = \text{Pt} + \text{CO}_2 + 2\text{HCl} + \text{CO}$.

When a solution of COPtCNS.KCNS (Foerster¹) is simply evaporated, the carbon monoxide is set free, and COPtS (Foerster²) is decomposed by reduced pressure. All the compounds of the types COPtCl_2 , $\text{COPt(R)}_2.2\text{HCl}$, $(\text{CO})_2\text{Pt(R)}_2.2\text{HCl}$ (R = residue of ammonia or primary



base), COPtCNS , COPtS , etc. (Foerster³), are decomposed by the action of potassium cyanide, carbon monoxide appearing as such.

From this very brief review I am sure we can detect great similarity between dicarbonyl cuprous chloride and these compounds, a similarity so great that one could not fail to classify it with them as a true chemical compound.

To the compound $(\text{CO})_2\text{CuCl}_2.4\text{H}_2\text{O}$ I have given the name

¹ Ber. d. chem. Ges., 24, 2424,

² Loc. cit.

³ Loc. cit.

dicarbonyl cuprous chloride, this being in accord with the name given by Schützenberger to the analogous compound, $(\text{CO})_2\text{PtCl}_2$.

Conclusions.

1. Carbon monoxide is not absorbed by dry cuprous chloride. It is absorbed by cuprous chloride when in hydrochloric acid solution or suspended in water.

2. As a result of this absorption a compound of definite composition is formed. This is represented by the formula $\text{Cu}_2\text{Cl}_2 \cdot 2\text{CO} \cdot 4\text{H}_2\text{O}$.

3. This compound conducts itself like a true atomic compound. It is decomposed by reduction of pressure or elevation of temperature, these decompositions being similar to the decompositions of compounds, the true atomic nature of which cannot be doubted.

4. The carbon monoxide shows no marked increase in chemical activity at the moment of liberation from the compound.

5. From a comparison of dicarbonyl cuprous chloride with other inorganic compounds containing carbon monoxide, it is found to conduct itself in a manner similar to them, and deserves to be ranked as a true chemical compound.

BIOGRAPHICAL SKETCH.

William App Jones was born in Hillsboro, N. C., Nov. 24, 1873. His early training was received in the private schools of that place. In 1886 he entered Moravian Falls Academy, and after three years of preparatory study entered Wake Forest College (N. C.), from which institution he received the degree of bachelor of arts in 1893. After being in business for a year he returned to his alma mater, where he spent a year in the study of chemistry. In 1895 he entered the Johns Hopkins University, where he has since devoted himself to the study of chemistry, geology, and mineralogy. In the spring of 1897 he was appointed a fellow in chemistry, and since Jan., 1898, he has acted as lecture assistant to Prof. Remsen.

